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Studies on molecular interaction in ternary liquid mixtures by ultrasonic velocity measurements

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Abstract : Adiabatic compressibility, intermolecular free length, free volume and internal pressure and their excess values have been obtained from the measurement of ultrasound velocity in three ternary liquid systems with benzene as the common component The nature and extent of molecular interaction have been discussed in terms of the excess values An attempt has been made to correlate the experimental ultrasonic velocity with those predicted on the basis of collision factor theory (CFT) and free length theory (FLT) with a view to compare the merits of the same The chi-square test for goodness of fit is applied to check the validity of the theories. The molecular interaction parameter (α) is also calculated and found to be useful in understanding the interaction in ternary liquid systems.

Keywords : Excess acoustical parameters, molecular interaction, chi-squared test

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1. Introduction

The study of intermolecular interactions is of considerable importance in the elucidation of the formation of complexes and plays an important role in the liquid mixtures [1,2]. The intermolecular interactions influence the structural arrangement along with the shape of molecules. Lagemann and Dunbar [3] was the first to point out the sound velocity approach for qualitative determination of the degree of association in liquids. Attempts have been made by Fort and Moore [4], Kaulgud [5] and Prasad *et al* [6,7] to study the behaviour of binary liquid mixtures by measuring the sound velocity and related properties, but, only a few investigations have been carried out in ternary liquid mixtures [8–10]. The present paper reports the results of the ultrasonic study of molecular interaction in the following ternary liquid mixtures : (i) Benzene-Ethyl alcohol-Chlorobenzene, (ii) Benzene-Ethyl alcohol-Bromobenzene, (iii) Benzene-Ethyl alcohol-Acetophenone.

Another aim of the present work is to compare the experimental ultrasonic velocity with those evaluated using the free length theory (FLT) suggested by Jacobson's [11] and collision factor theory (CFT) due to Schaaff's [12]. The molecular interaction term (α) has also been calculated for all the mixtures and discussed in the light of interactions which are known to exist.

2. Experimental

Ultrasonic velocity for the mixtures has been measured at 3 MHz using an interferometer with an accuracy of ± 0.1%. The temperature was maintained at 30°C ± 0.1°C by an electronically controlled thermostat. The viscosities of mixtures were obtained using Ostwald's Viscometer.

3. Theory

The adiabatic compressibility β_{ad} [13,14], free length L_f [15], free volume V_f [16] and the internal pressure π_i [17] were calculated using the following relations :

$$\beta_{ad} = \left(U^2\rho\right)^{-1}, \tag{1}$$

$$L_f = K\beta_{ad}^{1/2}, \tag{2}$$

$$V_f = \left(\frac{MU}{K\eta}\right)^{3/2}, \tag{3}$$

$$\pi_i = \left(\frac{[bRT]^3}{V_f}\right)\cdot\frac{1}{\nu^2}. \tag{4}$$

The excess parameters A^E can be calculated from the relations

$$A^E = A_{\text{exp}} - A_{\text{ideal}} \tag{5}$$

and $$A_{\text{ideal}} = X_1A_1 + X_2A_2 + X_3A_3$$

where the symbols have their usual significance.

The sound velocity in all the systems have been evaluated on the basis of free length theory [11] due to Jacobson and Collison factor theory [12] due to Schaaff.

Molecular interaction (α) :

The degree of intermolecular interaction (α) is given by,

$$\alpha = \frac{U^2\ \text{exp}}{U^2\ \text{im}} - 1, \tag{6}$$

where U_{im} is calculated following the equation suggested by Van Dael and Vangeel (18) given by

$$\frac{1}{X_1M_1 + X_2M_2 + X_3M_3}\ \frac{1}{U^2\text{im}} = \frac{X_1}{M_1U_1^2} = \frac{X_2}{M_2U_2^2} = \frac{X_3}{M_3U_3^2}, \tag{7}$$

where M and U stands for the molecular weight and ultrasonic velocity respectively and suffixes 1, 2 and 3 refer to mixture components.

4. Chi-squared test for goodness of fit

The chi-squared test of goodness of fit [19] enables us to determine if the deviation of the experiment from theory is chance or is due to the inadequacy of the theory to fit the observed data.

If Ei (i = 1, 2... n) is a set of observed (experimental) frequencies and Ti (i = 1, 2... n) is the corresponding set of expected (theoretical) frequencies, then Karl Pearson's chi-square given by

$$\text{Chi-square } (\chi)^2 = \left[\frac{(Ei - Ti)^2}{Ti}\right] \tag{8}$$

follows chi-square distribution with (n–1) degrees of freedom.

The tabulated value of chi-squared at 1% level of significance is 13.277. If the chi-square value calculated using eq. (8) is less than the tabulated value of chi-square for the same degrees of freedom then there is good correspondence between theory and experiment.

5. Results and discussion

Table 1 presents the excess values of viscosity, adiabatic compressibility, free length, free volume and internal pressure for all the three ternary liquid mixtures. The measurement of viscosity in ternary mixture can give some reliable information in the study of molecular interaction. Table 1 shows that the excess viscosity is negative throughout the whole range of concentrations in all the systems studied and decreases with increase in concentration of third component. The large negative values of excess viscosity for all the systems can be attributed to the presence of dipolar forces [20] between the components.

The excess values of compressibility and free length are negative for all the systems and both increase with the increase in concentration of chlorobenzene in system I, bromobenzene in II and acetophenone in III and reach a maximum value at 0.3 mole fraction and then gradually decrease. The reduction in compressibility and free length as well as the negative excess values clearly indicate that the existence of molecular interactions. According to Ramamoorthy and Sastry [21], the negative excess free length indicates that the sound wave needs to cover a larger distance. This may be attributed to dominent nature of interactions between unlike molecules. Srivastava and Dubey [22] also

arrived at a similar conclusion on the basis of excess values of compressibility. This view supports the present investigation.

Table 1. Values of excess viscosity, excess adiabatic compressibility, excess free length, excess free volume and excess internal pressure at 303 K

Mole fraction		Excess viscosity	Excess adiabatic compressibility	Excess free length	Excess free volume	Excess internal pressure
X_2	X_3	η^E ($\times 10^{-3}$ poise)	β_{ad}^E ($\times 10^{-9}$ m^2/N)	L_f^E (A°)	V_f^E ($\times 10^{-6}$ m^3)	π_i^E (atmos)
System I Benzene (X_1)-Ethylalcohol (X_2)-Chlorobenzene (X_3)						
0.4601	0 0935	–0 1760	0 00277	0.00232	–0.0193	–1422.95
0 3683	0 1858	–0 1382	–0 01277	–0 00309	–0 0201	–1260.30
0.2781	0 2780	–0.1020	–0.01142	–0 00260	–0 0196	–1009.43
0 1883	0.3690	–0 1016	–0.01489	–0.00409	0.0006	– 815.88
0.0923	0.4635	–0 0564	–0 00509	–0.00082	0.0018	– 433.85
System II · Benzene (X_1)-Ethylalcohol (X_2)-Bromobenzene (X_3)						
0 4623	0 0921	–0.1921	–0.01810	–0.00477	–0 0086	–1521.32
0.3680	0 1855	–0 1538	–0 02095	–0.00540	–0 0080	–1314.01
0.2786	0.2777	–0 1209	–0.02472	–0.00684	–0 0055	–1061.78
0.1891	0 3673	–0.1050	–0.01916	–0.00486	0 0036	– 813 93
0 0921	0 4617	–0 0788	–0.00486	0.00031	0.0091	– 453.08
System III . Benzene (X_1)-Ethylalcohol (X_2)-Acetophenone (X_3)						
0 4635	0 0925	–0 2057	–0.04189	–0 01308	–0 0069*	–1497.47
0 3704	0.1860	–0 1966	–0 05129	–0 01612	0.0019	–1342 89
0.2809	0.2757	–0.1802	–0 06216	–0 02042	0.0020	–1112 92
0 1866	0 3682	–0 1622	–0 05678	–0 01888	0.0037	– 817.74
0 0954	0.4601	–0 1436	–0.04746	–0 01600	0.0043	– 483.80

The values of excess free volume in all the mixtures are found to be both positive and negative. The excess free volume is negative when the mole fraction of third component is low and becomes positive when the concentration of the same is increased. The nature of sign changes when the mole fraction of third component is increased in all the systems. This is due to the weakening of the molecular interaction between the molecules of the systems. Such a behaviour is also noticed by Singh and Bhatti [23] in some ternary liquid mixtures. The negative excess internal pressure tending towards the positive values clearly confirms this view.

Normally, the dispersion forces make a positive contribution to the excess values while dipole-dipole, dipole induced dipole, charge transfer interaction and hydrogen bonding between unlike components make negative contributions. Observation of the negative excess internal pressure in mixture may be due to dipole-dipole interactions.

Table 2 shows the ultrasonic velocity evaluated using CFT and FLT relations along with the experimental velocity and the molecular interaction parameter (α). Table 3 lists the

Table 2. Ultrasonic velocity calculated theoretically and experimentally for different liquid mixture and the molecular interaction (α).

Mole fraction		U_{exp} m/s	U_{CFT} m/s	U_{FLT} m/s	
X_2	X_3				
System I : Benzene (X_1)-Ethylalcohol (X_2)-Chlorobenzene (X_3)					
0.4601	0.0935	1212.3	1221.35	1246.10	0 0880
0 3683	0.1858	1224 2	1227.26	1250.79	0 1139
0 2781	0.2780	1231 2	1233.07	1254.32	0 1153
0 1883	0.3690	1238.7	1238 87	1256 95	0 1010
0.0923	0 4635	1242.3	1245.05	1258.93	0 0591
System II · Benzene (X_1)-Ethylalcohol (X_2)-Bromobenzene (X_3)					
0 4623	0.0921	1198.2	1210 82	1228 09	0.1211
0 3680	0 1855	1181.3	1206.37	1217.03	0 1387
0.2786	0.2777	1172.3	1201 74	1206.60	0.1433
0 1891	0 3673	1165 4	1197.41	1197 17	0.1242
0 0921	0 4617	1155 9	1192 89	1187 88	0 0707
System III · Benzene (X_1)-Ethylalcohol (X_2)-Acetophenone (X_3)					
0 4635	0 0925	1259 3	1240 59	1238.33	0 1694
0 3704	0.1860	1288.2	1266 12	1238 99	0 2175
0.2809	0 2757	1322.6	1278 69	1241.89	0 2529
0.1866	0 3682	1347.5	1316.03	1247.92	0.2401
0 0954	0 4601	1369 9	1341 30	1256.92	0.1949

greater percentage deviations of the theoretical velocities from experimental values and values of chi-squared calculated using equation (14) for CFT and FLT. From Table 3 it is clear that the percentage deviation using CFT and FLT for system I is minimum (chi-squared is also minimum) whereas for system III it is greatest (chi-squared is also maximum). The system II shows intermediate percentage deviations (chi-squared is also intermediate). The chi-squared values obtained (Table 2) are less than the standard chi-squared at 1% level of significance except for the system III using FLT. This shows good agreement between experimental and theoretical values of ultrasonic velocities and hence the overall validity of the theories. The large deviation in the system III is mainly due to the association effects that are not taken into the theories. For all the systems, it is found that the CFT is best suited for the evaluations of ultrasonic velocity than the FLT [24].

From Table 2 it is observed that the maximum value of α (0.1153 in system I, 0.1433 in system II and 0.2529 in system III) occurs at the same concentration of third component in all the cases. The high positive values of α in the mixtures can be attributed to the existance of a weak dipolar interaction [25] between the molecules of the system.

Further the maximum values of α suggest the degree of molecular interaction in the respective systems under the present investigation.

Table 3. Greatest percentage deviation of theoretical velocities from experimental values and chi-squared from eq. (8).

Mixture	Maximum percentage deviation (%)		Values of chi-squared	
	CFT	FLT	CFT	FLT
Benzene-Ethylalcohol-Chlorobenzene	0.74	2.71	0.08	2.39
Benzene-Ethylalcohol-Bromobenzene	3.10	2.94	3.38	4.46
Benzene-Ethylalcohol-Acetophenone	3.32	8.25	3.52	25.66

6. Conclusion

The excess ultrasonic properties and the molecular interaction term reveal that the presence of molecular interaction in all the systems. From the magnitude and the tendency to change in sign of the excess parameters, it may be concluded that a weak molecular interaction due to dispersion forces and dipolar action between the components of the mixture, exists. The chi-squared test confirms the validity of the theoretically predicted sound velocity in the systems studied.

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